Cleaning of carbon nanotubes near the π-plasmon resonance

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Abstract

The cleaning of bulk carbon single-walled nanotubes (SWNTs) by use of a 248 nm excimer laser is verified with imaging, and quantitative evaluation of morphology and composition. A 5% change in responsivity of a pyroelectric detector coated with SWNTs is presented as a novel assessment of the change in SWNT coating topology. Changes in purity are shown by reduced full-width-at-half-maximum of the Raman D-band for 248 nm exposure up to 755 mW/cm^2. The 248 nm (5 eV) photon–plasmon resonance is considered as a mechanism for the reduction of impurities and an intermediate stage of purification.
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In the recent past we have undertaken the development of novel thermal detectors with coatings made from carbon single-walled nanotubes (SWNTs) and carbon multiwalled nanotubes (MWNTs) [1,2]. Such coatings have the potential for high damage threshold, uniform spectral responsivity, and resistance to aging, and are of particular interest for laser measurements at 248, 193, and 157 nm. We are also interested in solving the larger problem of removing impurities from as-produced (AP) carbon nanotubes, because rapid and inexpensive purification is one of the critical barriers to industrial production and commercial application. Haddon et al. [3] summarized multiple steps of purification to achieve ever-higher levels of sample purity ranging from AP materials to the ultimate goal of obtaining SWNTs of known (or defined) length and chiral index. We use the term *cleaning* to refer to an early stage of purification whereby AP material is made free of catalyst, amorphous carbon, and other particles. Most purification techniques reported in the literature are based on a combination of thermal and chemical treatments such as HNO_3 [4,5], HCl [6,7] and mixtures of H_2SO_4/HNO_3 [8]. However, the complete separation of impurities from SWNTs is dif-

ficult; therefore, a compromise between purity and yield is inherent. Few investigations have considered laser treatment or thermalization of photons, much less photochemical processes [9]. We know of no other SWNT experiments where purification is undertaken with laser radiation at 248 nm (∼5 eV) with photon energy near the π-plasmon resonance, near 5 eV [10].

The SWNT samples for the present work were Carbolex® material produced by arc-discharge (arc), and CoMo-CAT® or HiPCO® materials produced by chemical vapor deposition (CVD) [11]. In each case, the SWNTs were dispersed in chloroform and applied to a substrate with an airbrush technique [1].

The basis of the cleaning experiments was a 248 nm laser operating with a pulse width of approximately 20 ns and a pulse repetition frequency of 10 Hz. The beam exiting the laser was spatially homogenized by means of two lenses in series. Each lens consisted of an array of cylindrical lenselets with the cylindrical axis of the first lens perpendicular to the second. The beam was an unpolarized homogeneous square, approximately 1×1 cm, as measured by a pyroelectric array detector. The SWNT sample was placed in the beam path after the average power was measured with a thermopile-based detector, calibrated by means of an isoperibol calorimeter. Each laser exposure was defined by opening a manual shutter for 30 s.

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The temperature of the SWNT samples was measured during laser exposure with an optical pyrometer. The manufacturer's specifications inform us that the pyrometer measurement is valid for a circular heated area that is approximately 7 mm in diameter or larger. The highest steady state temperature we measured was approximately 70 °C for a sample exposed to 480 mW/cm^2 for 30 s. This measurement was not intended as a precise, instantaneous measurement of the sample heating during laser exposure, but rather to assure ourselves that the average temperature was well below the temperature required for oxidation of the SWNTs.

SEM images of the sample material qualitatively confirm the initial presence of impurities (material that is apparently not SWNTs or SWNT bundles characterized by rope-like features). A sample image of AP CoMoCAT® SWNTs on a pyroelectric detector is shown in Fig. 1a. We also have found that mere visual observation correlates well with changes in composition and purity that are observed by SEM. Specifically, the SWNTs look visibly blacker after 248 nm laser treatment, which suggests less graphitic material and increased porosity that is clearly evident with SEM (Fig. 1b).

The spectral responsivity measurements were acquired by the method of direct substitution, which is documented elsewhere [12]. Recently, we have shown that the spectral responsivity of a pyroelectric detector coated with purified SWNT 'bucky paper' will exhibit optical properties that are characteristic of the dielectric function of the coating [13]. In terms of spectral responsivity measurement, from the standpoint of quantifying damage, we expected reduced responsivity as a result of material loss. However, the data in Fig. 2 shows that the responsivity increased after laser exposure for one minute. Becker et al. have shown that topology and extent of percolation will influence the absolute absorptivity of the detector coating [14]. Therefore, we attribute this increase in responsivity to greater porosity of the coating as apparent in Fig. 2 and, as discussed later, the removal of carbon impurities. Upon exposure to laser irradiance greater than 755 mW/cm^2 for one minute, the detector responsivity decreased as the SWNT material was nearly completely removed. From the spectral responsivity measurements, we have yet to achieve SWNT samples with
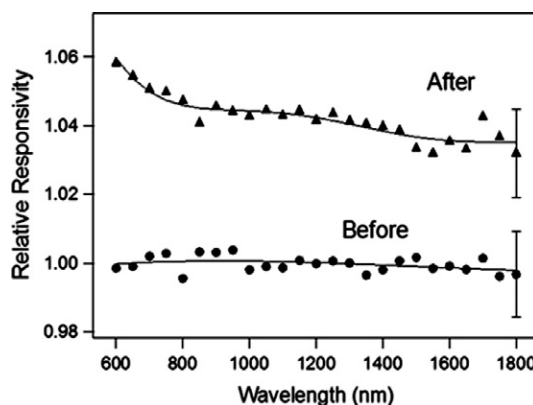

Fig. 2. Spectral responsivity of a SWNT coated LiTaO$_3$ pyroelectric detector taken before and after laser exposure. The uncertainty of the measurement is 1.25% with a 96% confidence interval. A representative error bar is shown. The lines are polynomial fits of the data intended only to guide the eye.

sufficient purity to resolve characteristic spectral shapes of metallic and semiconducting interband transitions. Thus it is difficult to quantify the purity of SWNTs by employing methods such as described by Landi et al. [10].

Resonant Raman spectroscopy (RRS) measurements were performed in the backscattering configuration using 7 mW of an argon ion laser providing 488 nm (2.54 eV) excitation. A 55 mm telephoto lens was employed both to focus the beam to ~0.25 mm^2 area and to collect the Raman scattered light. The scattered light was analyzed with a 0.27 m grating spectrometer equipped with a liquid nitrogen cooled charge-coupled detector and a holographic notch filter.

Information derived from RRS is important in terms of characterizing both the diameters of the SWNTs and the relative quantities of carbon impurities. The 'G-band' at 1500–1650 cm^{-1} is a compilation of bands originating from the in-plane vibrational modes of carbon in the curved graphite lattice, while the 'D-band' at ~1350 cm^{-1} is generated by symmetry lowering effects such as defects, tube ends or the presence of nanoparticle or amorphous carbons. A broad D-band is characteristic of the presence of non-nanotube carbon impurities [15]. The radial breathing modes (RBMs), which are less than 500 cm^{-1}, are dependent upon the diameter of the tube according to $d = 248/\omega_{RBM}$ [15], where d is the tube diameter and ω_{RBM} is wavenumber in units of nm and cm^{-1} respectively [15].

A partial summary of our 488 nm RRS of Carbolex® samples is shown in Fig. 3. In Fig. 3a (inset), RBMs normalized to the 154 cm^{-1} peak intensity shows that the diameter distribution does not change with increasing exposure to 248 nm laser power. Hence, SWNTs are not destroyed by laser treatment for 30 s with irradiances of 165–755 mW/cm^2. Dillon et al. have stated the full-width-at-half-maximum (FWHM) of the D-band of amorphous carbon and nano-crystalline graphite at 488 nm excitation are ~57 and 86 cm^{-1} [15]. The D-band FWHM of the as-received Carbolex® material (Fig. 3b) is 40 cm^{-1}, and
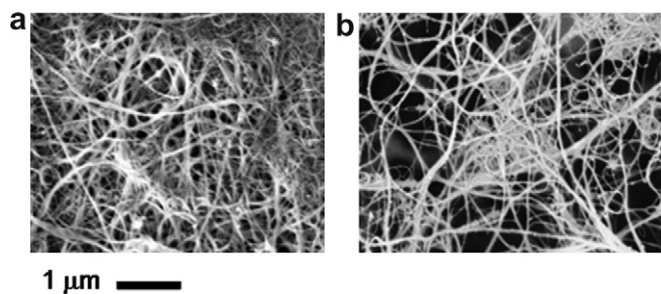

Fig. 1. SEM images of a LiTaO$_3$ pyroelectric detector coated with CoMoCAT® SWNTs taken (a) before and (b) after 1 min of 755 mW/cm^2 laser irradiation.
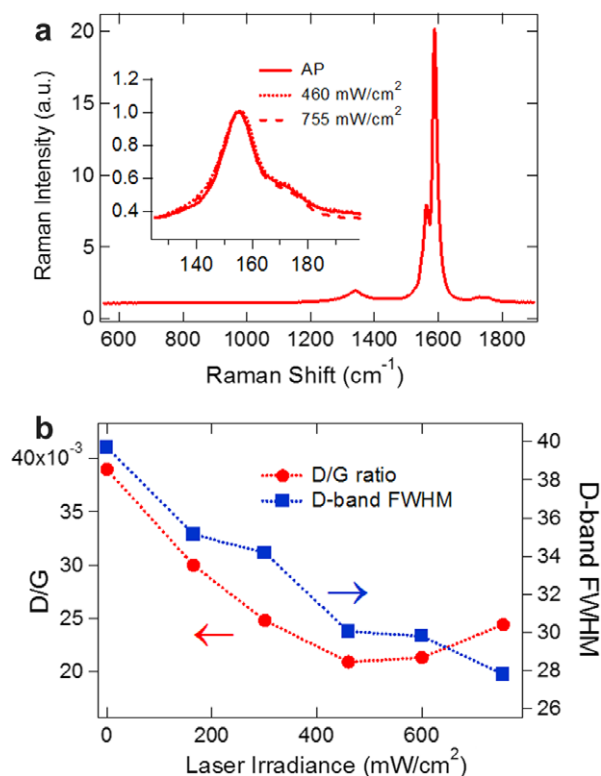
Fig. 3. (a) Raman spectrum at 488 nm for Carbolex® SWNTs exposed to 460 mW/cm^2 for 30 s inset are the RBMs for samples as-produced and after 248 nm laser exposure for 30 s at 460 and 755 mW/cm^2, and (b) the corresponding values for the FWHM D-band and the intensity of the D/G-band for increasing laser power.

decreases to 28 cm^{-1} with exposure to higher laser irradiance, indicating a reduction in carbon impurities such as amorphous carbon and nano-crystalline graphite. This is approaching that of documented samples of >98 wt% purified laser-generated SWNTs with a similar diameter distribution that contain relatively few carbon impurities and have a D-band FWHM in the range of 15–22 cm^{-1} [15].

Another important measure of purity is the ratio of the intensity of the D-band to that of the G-band, which is plotted against the left axis of Fig. 3b. The D/G ratio decreases for increasing irradiance in the range of 165–460 mW/cm^2, which is consistent with the elimination of impurity carbons as the relative intensity of the disorder band decreases. However, at greater values of laser irradiance, 600–755 mW/cm^2, the D/G ratio increases. In this regime, it is likely that the laser treatment creates defects in the nanotubes, without completely damaging or destroying the nanotubes but resulting in an increase in the SWNT D-band intensity. Since the tube ends are the most reactive part of the nanotube, it is possible that the laser treatment causes opening of the ends of the tubes. For longer exposure and fluences greater than 30 s, irradiation at 248 nm may result in the destruction of SWNTs.

Additional experiments were undertaken in a different atmosphere and using different SWNT material. We repeated the laser treatment experiments by exposing Car-

bolex® samples to irradiation in partial vacuum (7 × 10^{-4} Torr) and a less dramatic cleaning effect was observed in absence of oxygen as indicated by smaller decrease in the FWHM and change in D/G ratio. In addition, HiPCO® material purchased as 'purified' exhibits different D/G and D-band FWHM behavior. In particular, the FWHM decreases for exposures up to 200 mW/cm^2, then increases for higher power densities, while the D/G ratios remain nearly unchanged, which supports the observation that the conditions for cleaning vary for SWNTs synthesized by different processes [4]. The normalized RBMs for laser treated 'purified-grade' HiPCO® SWNTs indicates that tube diameters as small as 0.8 nm are sustained through the cleaning process for fluences 200–700 mW/cm^2.

Previous RRS studies have shown the evolution of SWNT Raman spectra as a function of exposure to laser radiation at 514.5 nm [16] and 632.8 nm [16,17]. These reports show a decrease in the D-band and the D/G ratio as well as a change in the diameter distribution with increasing laser power. These authors attributed the changes to in situ overall heating and oxidation of carbon impurities in addition to the oxidation of the smaller tubes in the sample. Our results are also in contrast to a chiral selective method where selective removal of SWNTs in resonance with 514.5 nm was attributed to the resonance with the interband transitions [18].

It is well known that 248 nm excimer laser excitation in the presence of oxygen creates ozone, which may play a role in the oxidation of carbon impurities in the SWNT sample. We have observed a relatively low average temperature increase during the SWNT exposure, but this does not eliminate the possibility that the apparent purification is the result of oxidation of carbon impurities resulting from laser heating and very high instantaneous temperature change with each laser pulse. Using a UV lamp to generate ozone, Simmons et al. reported an increase in the Raman D/G ratio of SWNTs with increasing exposure time for which the authors attributed the creation of defects in the side wall of nanotubes [19]. Ozone generated by 248 nm laser, in addition to the resonant heating of the π-plasmon of the nanotubes facilitates the oxidation of carbon impurities in the nanotube sample. The relative decrease in the D-band FWHM was only 7% in vacuum, yet in an air a decrease of 30% was observed at 710 mW/cm^2 and 755 mW/cm^2 respectively. Similarly, the greatest decrease in the D/G ratio in vacuum was 27% at 285 mW/cm^2; while in air the D/G decreased by 54% at 460 mW/cm^2. This suggests the important, but not exclusive role of oxygen in the cleaning mechanism. We do not observe any plasma ionization at the SWNT surface or the characteristic audible shock wave of laser-induced plasmas.

The π-plasmon resonance (for graphite as well as SWNTs) broadly overlaps the 248 nm (5 eV) excimer laser frequency [10]. Therefore, we believe laser irradiation of

SWNTs near 5 eV efficiently transfers momentum to the bonding orbitals of the impurities that are more defective and less stable than the SWNTs. As a result, carbon impurities in the AP–SWNT material readily react with oxygen or ozone in the surrounding air preferentially to dramatic heating or ionization near the SWNT coating surface. Lin et al. indicate that intertube Coulomb interactions significantly affect electronic excitations, so that the π-plasmons in nanotube bundles are different from those in a single nanotube [20]. Thus, it is also possible that the change in topology may be attributable to de-bundling (or simply a change in bundling). Finally, according to previous studies of laser vaporization of metals there is a basis for material removal when the plasmon resonance overlaps the photon excitation frequency [21,22].

From the standpoint of designing a thermal detector coating for excimer laser measurements, we have measured the enhancement of the coating absorptivity up to 755 mW/cm^2, but an apparent damage threshold for greater irradiance. However, laser damage, from the standpoint of detector design, may in fact be considered purification from the standpoint of SWNT post-processing. We have observed a change in the coating topology, and RRS studies have shown that exposure to 248 nm excimer laser radiation correlates with a reduction of non-nanotube carbon without destroying tubes or adding defects, up to an irradiance of approximately 600 mW/cm^2. Our experimental results are attributable to a unique interaction of the π-plasmon resonance in SWNT material with the 248 nm photons and demonstrate a simple method for removing carbon impurities from bulk AP–SWNTs.

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